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(54) **Process for the carbonylation of olefin.**

(57) The invention relates to a process for the carbonylation of olefins in which process an olefin is reacted with carbon monoxide in the presence of an alcohol or water and of a catalyst system, obtainable by combining:

(a) a metal of Group VIII or a compound thereof and

(b) a bidentate phosphine, arsine and/or stibine derivative, wherein as bidentate (b) a compound is selected having the general formula



wherein M^1 and M^2 are independently P, As or Sb, R is a divalent organic bridging group with at least 2 carbon atoms in the bridge, and R^1-R^4 represent the same or different optionally substituted tertiary alkyl groups. The invention further relates to a catalyst system suitable for this process.

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The invention relates to a process for the carbonylation of olefins by reaction with carbon monoxide in the presence of a catalyst system.

The invention in particular concerns the preparation of alkylpropionates which are commercially used as solvents and in flavouring compositions and perfumes.

5 Furthermore the invention relates to certain catalyst systems, suitable to be used in the carbonylation process.

Various processes for the carbonylation of olefins are already known. In order to improve the conversion of the olefin, the selectivity towards the desired product, or both, many modifications have been tried out which, although effective in one respect, are usually unfavourable in another aspect.

10 For example, in EP 279477 a continuous process for the carbonylation of an alkene is disclosed using a catalyst system comprising palladium or a palladium compound, a ligand, in particular triphenylphosphine and an acid, wherein the ligand and the acid are added either continuously or intermittently and whereby catalyst removed from the reaction vessel is recycled. Whereas in this process high selectivities with respect to the desired methylpropionate are obtainable, the consumption of catalyst components per kg
15 methylpropionate is relatively high notwithstanding the catalyst recycle step.

In other processes, e.g. the process described in US 3,168,553 catalyst systems comprising as metal component rhodium, ruthenium, iridium, or, in particular cobalt are used. With the aid of these catalyst systems, relatively low yields of the desired ester are obtained and moreover these processes are usually unattractive in view of the required high pressures.

20 According to another process, described in EP 411721, alkylpropionates can be produced continuously by reacting an alkanol in the liquid phase with ethene and carbon monoxide in the presence of a carbonylation catalyst and removing alkylpropionate from the reactor vessel in a stream of vapour. The catalyst is based on a palladium compound, a large excess of a phosphorus-, arsenic-, or antimony-containing ligand, in particular triarylphosphine and a protonic acid, e.g. sulphuric acid.

25 In the carbonylation process described in EP 55875, an olefin is reacted with carbon monoxide in the presence of water, an alcohol or a carboxylic acid. As catalyst a system is used comprising a palladium component or a cobalt-containing catalyst together with the palladium component, a tri-organophosphine promoter, containing at least one aliphatic carbon atom bonded to phosphorus. The molar ratio between the organophosphine and palladium is less than 10:1. In practice still relatively high molar ratios, e.g. of 6:1 or
30 7:1 are used.

In the non-published UK patent application (No. 9100801.1) a carbonylation process is described whereby use is made of a catalyst system comprising a source of palladium cations, a source of bidentate phosphine wherein the two phosphorus atoms are bonded to aliphatic groups, and a source of anions derived from a strong acid. The process is carried out in the presence of a hydride source and the
35 carbonylation products are mainly aldehydes and/or ketones.

It has now been found that in the carbonylation of olefins unexpected advantages are obtained, if the reaction is carried out in the presence of a catalyst system based on a ligand selected from a special group of bidentates. In many cases particularly high reaction rates are thus attained.

40 The invention can be defined as relating to a process for the carbonylation of olefins in which process an olefin is reacted with carbon monoxide in the presence of an alcohol or water and of a catalyst system, obtainable by combining:

- (a) a metal of Group VIII or a compound thereof and
- (b) a bidentate phosphine, arsine and/or stibine derivative, wherein as bidentate (b) a compound is selected having the general formula



45 wherein M^1 and M^2 are independently P, As or Sb, R is a divalent organic bridging group with at least 2 carbon atoms in the bridge, and R^1 - R^4 represent the same or different optionally substituted tertiary alkyl groups.

50 In the bidentate of formula I, M^1 and M^2 are preferably the same and in particular they both represent phosphorus atoms.

The bridging group R usually contains from 2 to 5 carbon atoms which may be substituted by one or more substituents such as alkyl groups, e.g. of 1 to 4 carbon atoms, alkoxy groups in which the alkyl group
55 comprises from 1 to 3 carbon atoms, dialkylamino groups in which the alkyl groups independently comprise 1 to 3 carbon atoms, or halogen atoms such as bromine and chlorine atoms.

In the bridging group the carbon chain may be interrupted by one or more heteroatoms such as oxygen or sulphur atoms, or by silano or dialkylsilicon groups in which the alkyl groups independently comprise

from 1 to 4 carbon atoms. Preferably the bridging group does not contain terminal heteroatoms.

Examples of suitable tertiary alkyl groups represented by R^1 to R^4 are tertiary butyl, 2-(2-methyl)butyl, 2-(2-ethyl)butyl, 2-(2-methyl)pentyl and 2-(2-ethyl)pentyl groups. In the present specification the alkyl groups represented by R^1 to R^4 include cyclic structures such as a 1-norbornyl or 1-norbornadienyl group.

5 Preferably the groups R^1 to R^4 represent the same secondary or tertiary alkyl groups.

A particularly preferred bidentate is 1,3-bis(di-tertiarybutylphosphino)propane.

Among the metals of Group VIII, cobalt, nickel, palladium, rhodium and platinum may be mentioned. Of these, palladium is in particular preferred. As source of Group VIII metal, hereinafter further exemplified as source of palladium, metallic palladium or, preferably, a palladium compound may be used, in particular a
10 palladium salt. Examples of suitable salts are salts of nitric acid, sulphuric acid, sulphonic acids such as methane sulphonic acid, chlorosulphonic acid, trifluoro methane sulphonic acid, a toluene sulphonic acid, e.g. p-toluene sulphonic acid, t-butyl sulphonic acid and sulphonated ion exchange resins.

Furthermore palladium salts of alkanolic acids may be used, in particular alkanolic acids with up to 12 carbon atoms, for example acetic acid, propionic acid or trifluoroacetic acid.

15 Preferred catalyst systems are based on palladium salts of strong acids, i.e. acids having a pKa value of at most 2.5, or a derivative thereof. Examples are trifluoroacetic acid and p-toluenesulphonic acids in combination with bidentates wherein at least two of R^1 to R^4 represent tertiary alkyl groups, in particular tertiary butyl groups. It is believed that such catalyst systems comprise palladium in cationic form.

The amount of acid may exceed the stoichiometric amount required for the palladium salt, if so desired.

20 Since halide ions can be corrosive, the source of palladium in the catalyst systems of the invention is preferably not a halide or a compound generating halide ions.

Conveniently the catalyst system of the invention is obtained by combining in a separate step, preceding the carbonylation reaction, the source of palladium and the bidentate of formula I. Suitably the palladium compound, as exemplified hereinbefore, is dissolved in a suitable solvent, and subsequently
25 admixed with the bidentate. The molar ratio between the bidentate (b) and the palladium source (a) is preferably in the range of 1:1 to 5:1 and, more preferably, in the range of 1:1 to 3:1. The possibility of applying these low molar ratios is advantageous, as it avoids the use of an excess of bidentate (b) and hence minimizes the consumption of these usually expensive compounds.

The amount of catalyst used in the process is not critical. Good results are obtained when the amount
30 of Group VIII metal is in the range of 10^{-7} to 10^{-1} gat per mole of olefinic double bond to be carbonylated. Preferably this amount is in the range of 10^{-5} to 5.10^{-2} gat per mole.

A wide range of olefins may be used in the process of the invention. Suitable olefins include those having 2 to 30 carbon atoms, in particular olefins with 2 to 12 carbon atoms per molecule. Preferably lower olefins are applied having from 2 to 6 carbon atoms, e.g. ethene, propene, butenes, and pentenes. Ethene
35 and propene are in particular preferred.

If desired olefins having more than one ethylenically unsaturated double bond may be used, in particular those wherein the double bonds are non conjugated, such as 1,5-hexadiene. Mixtures of olefins may be used, but in general product recovery is easiest if a single end product is aimed at.

Olefins wherein one or more hydrogen atoms have been replaced by inert substituents may also be
40 used. Examples of inert substituents are halogen atoms and cyano, ester, alkoxy, aryl, hydroxy, and carboxy groups. Olefins thus substituted are for example styrene and alkylesters of unsaturated carboxylic acids, such as methylacrylate.

If the carbonylation process is carried out in the presence of water, the product obtained will be a carboxylic acid. The acid may be converted into other products such as amides or esters.

45 In the process according to the invention, esters may be obtained directly, if the carbonylation is carried out in the presence of an alcohol.

Suitable alcohols include aliphatic mono alcohols, in particular those having from 1-5 carbon atoms per molecule such as methanol, butanol, isopropanol, and dihydric alcohols such as ethylene glycol and 1,3-propane diol.

50 Methanol is in particular preferred.

The amount of alcohol is not critical. Generally, amounts are used in excess of the amount of olefin to be carbonylated. Thus the alcohol may serve as reaction solvent as well, although, if desired, separate solvents may also be used.

In addition to a reaction solvent, if any, the reaction medium may contain one or more promoters.

55 Suitable promoters include organic oxidant promoters such as quinones and nitrocompounds. Moreover drying agents may be present such as trimethyl ortho formate.

The amount of promoter is not critical, but is conveniently related to the amount of catalyst used in the process. Accordingly the amount of promoter is usually in the range of 0.001 to 10 moles per mole of

olefinic double bond to be carbonylated, in particular in the range of 0.01 to 5 moles per mole.

The carbonylation reaction according to the invention is carried out at moderate temperatures and pressures. Suitable reaction temperatures are in the range of 50-250 °C, preferably in the range of 75-150 °C. Reaction temperatures outside these ranges may be applied, but generally do not offer special advantages.

The reaction pressure is usually at least atmospheric. Suitable pressures are in the range of 1 to 100 bar, preferably in the range of 5 to 50 bar.

The process may be carried out in batch operation or continuously. In embodiments relating to continuous operation of the process, products are conveniently stripped from the reaction mixture with the aid of a gas, usually feed gas, and subsequently recovered. The stripping gas is suitably returned to the reaction zone.

The carbon monoxide required for the reaction may be supplied in substantially pure form, or contaminated with in general minor amounts of inert compounds such as nitrogen, hydrogen and the like. The presence of sulphur containing contaminants such as COS or some metal compounds e.g. metal carbonyl compounds, should be avoided.

Hydrogen or a hydrogen containing gas may be present as a diluent for the carbon monoxide and other gaseous reactants. The pressure at which the hydrogen is supplied may vary, but is usually not more than that of the CO partial pressure.

The invention may be illustrated by the following Examples: Unless otherwise stated, all experiments were carried out in the following manner.

A 300 ml magnet-driven autoclave of Hastelloy C (Trade Mark) was charged with alkanol and further liquid and solid components of the reaction mixture as stated for each specific example. The catalyst components were dissolved in the respective solvent (usually the alkanol) under nitrogen atmosphere in a glove box and introduced in the nitrogen blanketed autoclave. The autoclave was closed, evacuated and subsequently pressurized with carbon monoxide and any other stated gaseous component. The autoclave was then heated to the indicated temperature and maintained at that temperature, usually for a period between 0.25 and 5 hours.

Finally the contents of the autoclave were analysed by gas-liquid chromatography.

Examples I to XIII

In Table I below the following data are indicated: the catalyst components present in the reaction mixture (in mmoles);

the alkanol and any further liquid (diluent) (in ml);

the olefin used and the pressures of the olefin, carbon monoxide and any other gas (in bar, unless otherwise mentioned);

the reaction temperature (in °C).

In Table II for each example the reaction rate (in moles of ester produced per gram of palladium and per hour) and the selectivity with respect to the desired product (in %) are shown.

Table I

Example No	Catalyst components (mmol)	Alkanol, etc. (ml)	olefin	Pressure (bar)	CO	other	Temperature (°C)
I	0.1 palladium acetate	40 butanol-1	ethene			H ₂	110
	0.3 1,3-bis(di-tert. butylphosphino)-propane						
	0.25 tert.butyl sulphonic acid		20	40	5		
II	0.1 palladium acetate	40 butanol-1	ethene		40	H ₂	110
	0.3 1,3-bis(di-tert. butylphosphino)-propane						
	0.25 methylsulphonic acid		20		5		
III	0.1 palladiumacetate	20 methanol	ethene				100
	0.3 1,3-bis(di-tert. butylphosphino)-propane						
	0.25 tert.butyl sulphonic acid		20	40			

Table I (Cont.)

Example No	Catalyst components (mmol)	Alkanol, etc. (ml)	Pressure (bar)			Temperature (°C)
			olefin	CO	other	
IV	0.1 palladiumacetate	20 methanol	ethene		H ₂	100
	0.3 1,3-bis(di-tert. butylphosphino)-propane	30 methylpropionate	20	40	5	
	0.25 methylsulphonic acid					
V	0.1 palladiumacetate	20 methanol	propene		H ₂	90
	0.3 1,3-bis(di-tert. butylphosphino)-propane	40 diglyme (dimethyl ether of di-ethylene glycol)	20 ml	30	30	
	0.25 methylsulphonic acid					
VI	0.1 palladiumacetate	50 methanol	octene-1			65
	0.3 1,3-bis(di-tert. butylphosphino)-propane	5 trimethyl orthoformate	(20 ml)	40		
	0.25 tert.butylsulphonic acid					

Table I (Cont.)

Example No	Catalyst components (mmol)	Alkanol, etc. (ml)	Pressure (bar)	Temperature (°C)
VII	0.1 palladiumacetate	30 methanol	styrene	75
	0.3 1,3-bis(di-tert-butylphosphino)propane		(20 ml)	
	0.25 tert.butylsulphonic acid		40	
VIII	0.1 palladiumacetate	10 water	ethene	90
	0.3 1,3-bis(di-tert-butylphosphino)propane	45 N-methylpyrrolidone	20	
	0.25 tert.butylsulphonic acid		40	
IX	0.25 palladiumacetate	40 methanol	methylacrylate	90
	0.6 1,3-bis(di-tert-butylphosphino)propane	5 trimethyl ortho-formate	(20 ml)	
	0.75 tert.butylsulphonic acid		40	

Table I (Cont.)

Example No	Catalyst components (mmol)	Alkanol, etc. (ml)	Pressure (bar)			Temperature (°C)
			olefin	CO	other	
X	0.25 palladiumacetate	40 methanol	methacrylate (20 ml)		H ₂	90
	0.6 1,3-bis(di-tert-butylphosphino)-propane			40	5	
	0.6 tert.butylsulphonic acid					
XI	0.25 palladiumacetate	50 methanol	acrylamide			115
	0.6 1,3-bis(di-tert-butylphosphino)-propane	5 trimethyl ortho-formate	(15 g)	40		
	0.6 tert.butylsulphonic acid					
XII	0.25 palladiumacetate	20 methanol	vinylacetate			75
	0.6 1,3-bis(di-tert-butylphosphino)-propane	40 diglyme	(20 ml)	40		
	0.5 tert.butylsulphonic acid					

Table I (Cont.)

Example No	Catalyst components (mmol)	Alkanol, etc. (ml)		Pressure (bar)		Temperature (°C)
				olefin	CO other	
XIII	0.25 palladiumacetate	50 methanol		cyanoethene		60
	0.6 1,3-bis(di-tert. butylphosphino)-propane	5 trimethyl ortho-formate		(20 ml)	40	
	1 trifluoromethylsulphonic acid					
A (comparative)	0.1 palladiumacetate	20 methanol		ethene		100
	3 triphenylphosphine	30 methylpropionate		20	40	
	2 methylsulphonic acid					
B (comparative)	0.1 palladiumacetate	20 methanol		ethene		100
	0.3 triphenylphosphine	30 methylpropionate		20	40	
	0.25 methylsulphonic acid					

Table II

Example No	Reaction rate (mol/gat.h)	Product selectivity (%)
I	11000	butylpropionate >98
II	10000	butylpropionate >98
III	5000	methylpropionate >98
IV	13000	methylpropionate >98
V	2000	methylbutanoate 86 methyl-(2-methylpro- pionate) 14
VI	100	methylester of n-octanecarboxylic acid 86 methylester of branched octanecarboxylic acid 14
VII	100	methylester of 1-phenylpropionic acid 88
VIII	1000	methylester of 2-phenylpropionic acid 12 propionic acid >98
IX	1500	dimethylsuccinate 98
X	3000	dimethylsuccinate 98

Table II (Cont.)

5	Example No	Reaction rate (mol/gat.h)	Product selectivity (%)
10	XI	400	methylester of mono amidosuccinic acid 75 succinimide 20
15	XII	200	1-acetoxy methyl propionate 40 2-acetoxy methyl propionate 60
20	XIII	30	2-cyano methyl propionate 95
25	A (Compara- tive)	400	methylpropionate 98
25	B	<10	methylpropionate (trace)

In the Tables two further examples are included for comparison only (Examples A and B).

Comparing the results of Example A with those of Example III, it will be clear that if instead of the bidentate catalyst component according to the invention, triphenylphosphine is used, large amounts thereof are required in order to achieve an acceptable reaction rate (Example A). If the phosphine is applied in an amount comparable to that used in Example III, the reaction rate is very low and only traces of methylpropionate are formed (Example B).

Another comparative experiment was carried out whereby the autoclave was charged with 10 ml methanol, 30 ml methylpropionate, 0.25 mmol palladiumacetate, 0.6 mmol 1,3-bis(di-sec.butylphosphino)-propane (instead of the bidentate of the invention) and 1 mmol tert.butylsulphonic acid. After flushing with carbon monoxide the reactor was pressurized with 20 bar ethene and 42 bar carbonmonoxide. The reaction temperature was maintained at 110 °C. After 3 hours the reaction was discontinued. 6 Gram of polymeric material (polyketones) had been formed. The selectivity with respect to methylpropionate was less than 30% (comparative Example C).

Claims

1. A process for the carbonylation of olefins in which process an olefin is reacted with carbon monoxide in the presence of an alcohol or water and of a catalyst system, obtainable by combining:

- (a) a metal of Group VIII or a compound thereof and
- (b) a bidentate phosphine, arsine and/or stibine derivative, wherein as bidentate (b) a compound is selected having the general formula



wherein M¹ and M² are independently P, As or Sb, R is a divalent organic bridging group with at least 2 carbon atoms in the bridge, and R¹-R⁴ represents the same or different optionally substituted tertiary alkyl groups.

2. A process as claimed in claim 1, characterized in that the bidentate of formula I is a bisphosphine wherein R¹-R⁴ represent the same tertiary alkyl groups.
3. A process as claimed in claim 1 or 2, characterized in that R¹-R⁴ represent tertiary butyl groups.
4. A process as claimed in one or more of claims 1-3, characterized in that the bidentate (b) is 1,3-bis(di-tert.butylphosphino)propane.
5. A process as claimed in one or more of claims 1-4, characterized in that the Group VIII metal is palladium.
6. A process as claimed in one or more of claims 1-5, characterized in that the molar ratio between (b) and (a) is in the range of 1:1 to 5:1.
7. A process as claimed in one or more of claims 1-6, characterized in that in the carbonylation reaction an olefin is used having from 2 to 30 carbon atoms being unsubstituted or substituted by one or more of the same or different substituents selected from halogen atoms, cyano, ester, alkoxy, aryl, hydroxy and carboxy groups.
8. A process as claimed in claim 7, characterized in that the olefin is an unsubstituted alkene having from 2 to 6 carbon atoms in particular ethene.
9. A process as claimed in one or more of claims 1-7, characterized in that the olefin is an ester of an unsaturated carboxylic acid.
10. A process as claimed in one or more of claims 1-9, characterized in that in the carbonylation reaction an aliphatic alcohol having from 1-5 carbon atoms is used.
11. A process as claimed in claim 10, characterized in that the alcohol is methanol.
12. A catalyst system comprising:
 - (a) a source of palladium cations
 - (b) a source of bidentate phosphine having the general formula I wherein M¹ and M² represents phosphorus atoms, R is a divalent organic bridging group with 3 carbon atoms and R¹-R⁴ are tertiary alkyl groups.
13. A catalyst system as claimed in claim 12 wherein R¹-R⁴ are tertiary butyl groups.

Process for the carbonylation of olefin.

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Abstract of EP 0495548 (A2)

The invention relates to a process for the carbonylation of olefins in which process an olefin is reacted with carbon monoxide in the presence of an alcohol or water and of a catalyst system, obtainable by combining: (a) a metal of Group VIII or a compound thereof and (b) a bidentate phosphine, arsine and/or stibine derivative, wherein as bidentate (b) a compound is selected having the general formula $R^1-R^2-M^1-R^3-R^4$; I wherein M^1 and M^2 are independently P, As or Sb, R is a divalent organic bridging group with at least 2 carbon atoms in the bridge, and R^1-R^4 represent the same or different optionally substituted tertiary alkyl groups. The invention further relates to a catalyst system suitable for this process. s

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